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# AQUEOUS-BASED ADHESIVE FOR BONDING LOW SURFACE ENERGY SUBSTRATES

## Background of the Invention

This invention relates to an aqueous-based adhesive for bonding low surface energy  
5 substrates. Polyolefins such as polyethylene and polypropylene and copolymers thereof are  
useful in the fabrication of many objects including automotive trim, shoe soles, toys, and  
household appliances. These polymers are inexpensive and lightweight and have excellent  
impact resistance. Unfortunately, the inherent low surface energy of polyolefins inhibits  
adhesion to most adhesive and coating formulations, which tend to contain polar materials  
10 such as urethanes, acrylics, and epoxies. Consequently, efforts have been directed toward pre-  
treating the surface of these low surface energy materials to render them adhesive. Such  
pretreatments include vapor cleaning, defatting, acid treating, priming, corona discharge  
treating, or plasma treating. Other efforts to improve adhesion have been directed to the use  
of adhesion promoters. Unfortunately, such techniques are often cumbersome, costly, and  
15 environmentally unsound. Accordingly, it would be advantageous to discover a simple way of  
applying adhesives to low surface energy substrates without surface pretreatment or adhesion  
promoters. It would further be advantageous for the adhesive or similar coating to be water  
based to reduce volatile organic content, odor, and cost.

## Summary of the Invention

20 The present invention addresses a need in the art by providing, in a first aspect, a  
2-part adhesive formulation comprising, in a first part, water, a surfactant, and a protected  
alkylborane complex and, in a second part, an acrylic monomer and a trialkylborane-displacing  
initiator.

In a second aspect, the present invention is a composition comprising water, a  
25 surfactant, an acrylic monomer, a trialkylborane-displacing initiator, and a thixotropic agent.

In a third aspect, the present invention is a method comprising the step of contacting a  
surfactant-stabilized aqueous dispersion of a trialkylborane-organonitrogen complex with a

acrylic monomer and a trialkylborane-displacing initiator to form a curing acrylic-based adhesive; and 2) applying the curing adhesive to a low surface energy substrate.

### Detailed Description of the Invention

In a first aspect, the present invention is a 2-part adhesive that comprises, in a first  
5 part, water, a surfactant, and a protected alkylborane complex and, in a second part, an acrylic monomer and a trialkylborane-displacing initiator. As used herein, the term "protected alkylborane complex" refers either to a trialkylborane-organonitrogen complex, which is an oxidatively stable complex of a trialkylborane and a nitrogen-containing organic compound, or a heterocyclic borate as described and taught in U.S. Patent 6,646,076, column 3, lines  
10 40-67 to column 4, lines 1-8, and columns 5-14, which description is incorporated herein by reference.

The preferred alkylborane complex is a trialkylborane-organonitrogen complex. The alkyl groups are preferably each independently C<sub>1</sub>-C<sub>10</sub>-alkyl or C<sub>1</sub>-C<sub>10</sub>-alkylcycloalkyl, more preferably C<sub>1</sub>-C<sub>5</sub>-alkyl. Examples of nitrogen-containing organic compounds include  
15 substituted or unsubstituted primary amines, secondary amines, tertiary amines, diamines, pyridines, pyrrolidines, pyrroles, and carbazoles.

Examples of preferred borane-organonitrogen complexes include triethylborane:dimethylaminopropylamine complex, tributylborane:dimethylaminopropylamine complex, triethylborane:pyrrolidine complex,  
20 tributylborane:pyrrolidine complex, triethylborane:pyridine complex, tributylborane:pyridine complex, triethylborane:isophorone diamine complex, triethylborane:isophorone diamine complex, tributylborane:isophorone diamine complex, triethylborane:methoxypropylamine complex, and tributylborane:methoxypropylamine complex.

The trialkylborane-organonitrogen complex can be prepared by contacting a  
25 trialkylborane compound, either neat or as a trialkylborane etherate complex, with a nitrogen-containing organic compound, preferably with a stoichiometric excess of the nitrogen-containing compound. For example, a preferred tri-*n*-butylborane:3-methoxypropylamine

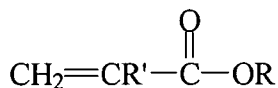
complex contains from about a 1:1.05 to about a 1:1.50 mole ratio of tri-*n*-butylborane to 3-methoxypropylamine.

The surfactant, which is a neutral or a basic surfactant or a combination thereof, is included in the first part of the 2-part formulation. Examples of suitable surfactants include  
5 polyvinyl pyrrolidinones, polyetheramines, polyethylene glycols, polyethylene glycol-polypropylene glycol copolymers, polyacrylamides, hydroxycellulosics, polyvinyl alcohols, polyacrylic acid salts, and polymethacrylic acid salts, and combinations thereof.

The concentration of surfactant in the first part of the formulation is sufficient to increase the shelf-stability of the complex in water, and varies depending on the surfactant  
10 used. In general, the concentration of the surfactant is in the range of from about 0.5 to about 25 weight percent, based on the weight of the surfactant, the water, and the complex.

The weight-to-weight ratio of water to the complex is preferably not less than 2:1, more preferably not less than 5:1, and most preferably not less than 10:1, and preferably not more than 100:1, more preferably not more than 50:1, and most preferably not more than 20:1.

15 The second part of the 2-part adhesive contains an acrylic monomer, a trialkylborane-displacing initiator and, optionally, a thixotropic agent. The term "acrylic monomer" is used herein to refer to an acrylamide monomer, an acrylonitrile monomer, or an acrylate monomer, with acrylate monomers being preferred. Acrylate monomers have the chemical structure:



20 where R is a substituent other than H; preferably alkyl, cycloalkyl, bicycloalkyl, or hydroxyalkyl, more preferably C<sub>1</sub>-C<sub>6</sub>-alkyl, isonorbonyl, or hydroxyethyl; and R' is a substituent, preferably hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl, more preferably hydrogen, methyl, or ethyl.

Examples of suitable acrylic monomers include acrylonitrile, acrylamide, *n*-methylacrylamide, methyl acrylate, ethyl acrylate, *n*-propyl acrylate, *n*-butyl acrylate, *t*-butyl  
25 acrylate, isobornyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl acrylate

and ethyl-*n*-hexyl acrylate, methyl methacrylate, ethyl methacrylate, *n*-propyl methacrylate, *n*-butyl methacrylate, *t*-butyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, isobornyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, and ethyl-*n*-hexyl methacrylate and combinations thereof.

- 5 More preferred acrylic monomers include 2-hydroxyethyl acrylate, hydroxybutyl methacrylate, and methyl methacrylate and combinations thereof. A most preferred acrylic monomer is methyl methacrylate.

- The trialkylborane-displacing initiator is characterized by its ability to displace the trialkylborane from the protected alkylborane complex, preferably the
- 10 trialkylborane:organonitrogen complex. Additionally, the initiator may be selected to be or to copolymerize with the acrylic monomer. Thus, the term "acrylic monomer and trialkylborane-displacing initiator" can refer to a single monomer that both initiates trialkylborane displacement and polymerizes or copolymerizes, or two or more separate compounds that, as a package, polymerize and initiate displacement. Examples of acrylic monomers that are also
- 15 trialkylborane-displacing initiators include 2-hydroxyalkylacrylates such as 2-hydroxymethylacrylate, 2-hydroxyethylacrylate, and 2-hydroxybutylacrylate.

- Examples of other suitable initiators include acids such as acetic acid, acrylic acid, methacrylic acid, formic acid, as well as isocyanates, aldehydes, ketones, acid chlorides, and anhydrides. Preferred initiators include acrylic acid and methacrylic acid and combinations
- 20 thereof. The amount of initiator used is preferably not less than 1, more preferably not less than 2 weight percent, and not more than 20, more preferably not more than 10 weight percent based on the weight of the initiator, the monomer, and the thixotropic agent.

- A thixotropic agent is an acrylic polymer that is advantageously included in the second part of the 2-part adhesive to adjust the viscosity of the second part to approximately match
- 25 the first part, preferably so that the first and second parts have viscosities that are within 20% of each other. Preferably, the amount of thixotropic agent used is not less than about 10 and not more than 30 weight percent based on the weight of the acrylic monomer, the borane-displacing initiator, and the thixotropic agent. A preferred thixotropic agent is a polymeric acrylic such as poly(methyl acrylate), poly(ethyl acrylate), poly(*n*-propyl acrylate),

poly(*n*-butyl acrylate), poly(*t*-butyl acrylate), poly(carboxyethyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-propyl methacrylate), poly(*n*-butyl methacrylate), poly(*t*-butyl methacrylate), and poly(carboxyethyl methacrylate). A more preferred thixotropic agent is poly(methyl methacrylate), which preferably has a weight  
5 average molecular weight ( $M_w$ ) of not less than 50,000, and more preferably not less than 75,000 Daltons, and preferably not greater than 500,000, and more preferably not greater than 400,000 Daltons.

The term "low surface energy substrate" is used herein to refer to a polymeric hydrocarbon, a polymeric fluorocarbon, or a polymeric hydrofluorocarbon substrate that does  
10 not include polar substituents. Examples of low surface energy substrates include polyethylenes, polypropylenes including isotactic and syndiotactic polypropylenes, ethylene- $\alpha$ -olefin copolymers including as ethylene-1-octene- and ethylene-1-butene-copolymers, hydrogenated polyisoprene (also known as poly(ethylene-*alt*-propylene)), polyvinylidene fluorides, polytetrafluoroethylenes, polyesters, polyamides, polyacetals, polystyrenes, and  
15 blends thereof.

Ancillary additives such as pigments, dyes, inorganic fillers, UV stabilizers, peroxides, organic solvents, and antioxidants may be included in either or both of the parts of the 2-part formulation. The adhesive, therefore, has further applicability as a paint, a primer, or a coating.

20 The second aspect of the present invention is a composition comprising water, a surfactant, an acrylic monomer, a trialkylborane displacing initiator, a thixotropic agent, and, optionally, one or more ancillary additives. This composition can be combined with the trialkylborane:organoamine complex and transferred to a single-head sprayer and applied to a substrate to make an adhesive, a paint, a primer, or a coating. Alternatively the components  
25 may be kept separate and applied through a plural component sprayer.

The third aspect of the present invention is a method comprising the steps of contacting the two parts of the 2-part formulation to provide a curing adhesive and applying the curing adhesive to the substrate. The steps of contacting the parts together may be distinct



or concomitant, and is preferably concomitant, that is, the two parts of the adhesive are brought into contact with each other, for example, using a bicartridge caulk gun at about the same time these components are contacting the substrate. The method of the present invention provides a simple way to apply an adhesive to a low surface energy substrate at  
5 room temperature without the aid of any surface pretreatment.

The following examples are for illustrative purposes only and are not intended to limit the scope of the invention. H29A refers to tri-*n*-butylborane:3-methoxypropylamine, containing an approximately 1:1.05 mole ratio of tri-*n*-butylborane to 3-methoxypropylamine; H29B refers to tri-*n*-butylborane:3-methoxypropylamine, containing an approximately 1:1.3  
10 mole ratio of tri-*n*-butylborane to 3-methoxypropylamine; pphp refers to parts per hundred parts by weight.

#### Example 1 – Preparation of Water-Borne Adhesive with H29A Stabilized with Polyvinylpyrrolidinone

A water-borne adhesive for bonding plastic substrates was prepared by combining at  
15 room temperature 3 parts of an acrylic resin consisting of 66.7 pphp methyl methacrylate (MMA), 17.3 pphp poly(methyl methacrylate) (PMMA,  $M_w = 300,000$  Daltons), 12 pphp 2-hydroxyethyl acrylate and 4 pphp acrylic acid with 1 part of a component consisting of 60 pphp water, 24 pphp polyvinylpyrrolidinone ( $M_w = 300,000$ ) and 16 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick  
20 coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours. Testing was performed on an Instron 4201 load frame with a 1000 lb load cell using Series 9 software supplied by the manufacturer. Upon testing the samples the substrate failed at 655psi +/-  
25 50 psi at an average elongation of 0.19 " for a 0.5 inch bond overlap.

## Example 2 - Preparation of Water-Borne Adhesive with H29A Stabilized with Polyvinyl alcohol

A water-borne adhesive for bonding plastic substrates was prepared by combining at room temperature 2 parts of an acyclic resin consisting of 62 pphp MMA, 16 pphp PMMA (M<sub>w</sub> = 300,000), 16 pphp 2-hydroxyethyl acrylate and 6 pphp acrylic acid with 1 part of component consisting of 85 pphp water, 11 pphp polyvinyl alcohol (M<sub>w</sub> = 150,000 ), and 4 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear samples failed by substrate failure with an average lap shear energy of 875 psi +/- 140 psi with an average elongation of 0.47 inches for a 0.5 inch substrate overlap.

## Example 3 - Preparation of Water-Borne Adhesive with PEG

A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin consisting of 72 pphp MMA, 18 pphp PMMA (M<sub>w</sub> = 300,000), 10 pphp acrylic acid with 1 part of a component consisting of 58 pphp water, 33 pphp polyethylene glycol (PEG, M<sub>w</sub> = 20,000), and 9 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear sample failed by substrate failure at a lap shear energy of 429 psi after elongating 0.14 inch for a 0.5 inch overlap.

## Example 4 - Water-Borne Adhesive with H29A stabilized with Polyetheramine

A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acyclic resin as described in Example 3 with 1 part of a component consisting of 70 pphp water, 25 pphp Jeffamine™ 2000, polyetheramine

(trademark of Huntsman Chemical), and 5 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration.

- 5 The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear specimens failed by substrate failure at a lap shear energy of 605 psi +/- 70 psi after elongating 0.25" for a 0.5 inch overlap.

#### Example 5 – Water-Borne Adhesive with H29A Stabilized with Sodium Salt of Polyacrylic Acid

- 10 A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin component as described in Example 3 with 1 part of a component consisting of 75 pphp water, 20 pphp of a fully neutralized sodium salt of polyacrylic acid ( $M_w = 30,000$ ) and 5 pphp of H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic
- 15 polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear specimens failed by substrate failure at a lap shear energy of 790 psi +/- 70 psi after elongating 0.33 inches for a 0.5 inch overlap.

- 20 Example 6 - Water-Borne Adhesive with H29A Stabilized with polyacrylamide

- A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin similar to that described in Example 3 with 1 part of a component consisting of 75 pphp water, 20 pphp polyacrylamide ( $M_w = 10,000$ ), and 5 pphp H29A. The components were manually mixed with a spatula and applied to
- 25 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to

cure for 24 hours and tested as described in Example 1. The resulting lap shear specimen failed by substrate failure at a lap shear energy of 690 psi.

#### Example 7 - Water-Borne Adhesive using Isophorone Diisocyanate Initiator

5 A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin similar to that described in Example 3 except that isophorone diisocyanate was substituted for acrylic acid with 1 part of a component identical to that water containing component described in Example 6. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive  
10 to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear specimen failed within the adhesive at a lap shear energy of 284 psi.

#### Example 8 - Water-Borne Adhesive with H29A Stabilized with a Polyethylene Glycol

15 A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin consisting of 65 pphp MMA, 20 pphp hydroxy butylmethacrylate, 10 pphp PMMA ( $M_w = 300,000$ ), 5 pphp acrylic acid with 1 part of a component consisting of 90 pphp water, 5 pphp Polyox™ N 80 polyethylene glycol (a trademark of The Dow Chemical Company), and 5 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524  
20 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear specimen failed in the substrate at a lap shear energy of 600 psi +/- 100 psi.

#### 25 Example 9 - Water-Borne Adhesive with H29A Stabilized with Teflon™ PFA Fluoropolymer

A water borne adhesive for bonding plastic substrates was prepared by combining at room temperature 1 part of an acrylic resin as described in Example 3 with 1 part of a

component consisting of 95% of a Teflon™ PFA fluoropolymer (Teflon is a trademark of DuPont) water dispersion (54% solids) and 5 pphp H29A. The components were manually mixed with a spatula and applied to 1" x 4" x 0.125" thick coupons of Basel 6524 isotactic polypropylene. Spacer beads with 0.005" diameter were applied to the surface of the adhesive to provide a uniform bead thickness and the laminate fixtured in a lap shear configuration. The laminate was allowed to cure for 24 hours and tested as described in Example 1. The resulting lap shear specimen failed cohesively in the adhesive at a lap shear energy of 489 psi +/- 20 psi.

#### Example 10 – Water-Borne Coating with H29B Stabilized with a Poly(acrylic acid)

A low surface energy curable paint was prepared by combining at room temperature 38.5 pphp water, 30 pphp MMA, 8.5 pphp 2-hydroxyethyl acrylate, 4.3 pphp polyacrylic acid, 1.7 pphp copper II phthalocyanine blue dye, 4.5 pphp acrylic acid, 8.5 pphp polymethyl methacrylate-co-ethyl acrylate ( $M_w$  101,000, < 5% ethyl acrylate obtained from Aldrich Chemical Milwaukee, WI). This resin mixture was pre-mixed by rolling to provide a homogeneous emulsion. This blend was combined with 4.5 pphp H29B and stirred for 30 seconds. The resultant curing paint formulation was spray applied to the surface of isotactic polypropylene coupon at a thickness of 3 mils and allowed to cure for 48 hours. The painted surface was then tested for adhesion by ASTM crosshatch method D 3359-83. The coating exhibited no adhesion failure.

#### Example 11 – Water-Borne Coating with H29B Stabilized with a Poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol)bis(2-aminopropyl ether)

A low surface energy curable paint was prepared by combining at room temperature 34.85 pphp water, 31.15 pphp MMA, 9.1 pphp 2-hydroxyethyl acrylate, 5.1 pphp Poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol)bis(2-aminopropyl ether), 1.7 pphp copper II phthalocyanine blue dye, 4.5 pphp acrylic acid, 9.1 pphp polymethyl methacrylate-co-ethyl acrylate ( $M_w$  101,000, < 5% ethyl acrylate obtained from Aldrich Chemical Milwaukee, WI). This resin mixture was pre-mixed by rolling to provide a homogeneous emulsion. This blend was combined with 4.5 pphp H29B

and stirred for 30 seconds. The resultant curing paint formulation was spray applied to the surface of isotactic polypropylene coupon at a thickness of 3 mils and allowed to cure for 48 hours. The painted surface was then tested for adhesion by ASTM crosshatch method D 3359-83. The coating exhibited no adhesion failure.

5    Example 12 – Water-Borne Coating with H29B Stabilized with a Polyacrylamide

          A low surface energy curable paint was prepared by combining at room temperature 29.85 pphp water, 31.05 pphp MMA, 9.1 pphp 2-hydroxyethyl acrylate, 10.2 pphp Polyacrylamide, 1.7 pphp copper II phthalocyanine blue dye, 4.5 pphp acrylic acid, 9.1 pphp polymethyl methacrylate-co-ethyl acrylate ( $M_w$  101,000, < 5% ethyl acrylate obtained from Aldrich Chemical Milwaukee, WI). This resin mixture was pre-mixed by rolling to provide a homogeneous emulsion. This blend was combined with 4.5 pphp H29B and stirred for 30 seconds. The resultant curing paint formulation was spray applied to the surface of isotactic polypropylene coupon at a thickness of 3 mils and allowed to cure for 48 hours. The painted surface was then tested for adhesion by ASTM crosshatch method D 3359-83. The coating exhibited no adhesion failure.

WHAT IS CLAIMED IS:

1. A 2-part adhesive formulation comprising, in a first part, water, a surfactant, and a protected alkylborane complex and, in a second part, an acrylic monomer and a trialkylborane-displacing initiator.
- 5 2. The formulation of Claim 1 wherein protected alkylborane complex is a trialkylborane-organonitrogen complex the second part further includes an acrylic polymer as a thixotropic agent.
3. The formulation of Claim 2 wherein the thixotropic agent is a poly(methyl methacrylate).
- 10 4. The formulation of Claim 3 wherein the surfactant is a polyvinyl pyrrolidone, a polyetheramine, a polyethylene glycol, a polyethylene glycol-polypropylene glycol copolymer, a polyacrylamide, a hydroxycellulose, a polyvinyl alcohol, a polyacrylic acid salt, or a polymethacrylic acid salt, or a combination thereof.
- 15 5. The formulation of Claim 3 wherein the second part of the formulation includes an acrylic monomer selected from the group consisting of hydroxyethyl acrylate, hydroxybutyl methacrylate, and methyl methacrylate; and a trialkylborane initiator selected from the group consisting of acrylic acid and methacrylic acid.
6. The formulation of Claim 5 wherein the acrylic monomer includes methyl methacrylate and the trialkylborane initiator includes acrylic acid.
- 20 7. A 2-part adhesive formulation comprising, in a first part, water, a surfactant, and a trialkylborane-organonitrogen complex and, in a second part, methyl methacrylate, a thixotropic agent, and a trialkylborane-displacing initiator selected from the group consisting of acrylic acid, methacrylic acid, and a 2-hydroxyalkyl acrylate.
- 25 8. The 2-part adhesive of Claim 7, which includes in either the first or second part or both a pigment, a dye, a filler, or an antioxidant, or a combination thereof.

9. A composition comprising water, a surfactant, an acrylic monomer, a trialkylborane-displacing initiator, and a thixotropic agent.
10. The composition of Claim 9 which further includes a protected alkylborane complex.
- 5 11. The composition of Claim 10 wherein the protected alkylborane complex is a trialkylborane-organonitrogen complex.
12. The composition of Claim 10 which forms a cured adhesive.
13. A method comprising the step of contacting a surfactant-stabilized aqueous dispersion of a trialkylborane-organonitrogen complex with a acrylic monomer and a trialkylborane-displacing initiator to form a curing acrylic-based adhesive; and 2) applying the curing adhesive to a low surface energy substrate.
- 10
14. The method of Claim 13 wherein steps 1) and 2) are carried out concomitantly.
15. The method of Claim 13 wherein the the low surface energy substrate is selected from the group consisting of polyethylenes, polypropylenes, ethylene- $\alpha$ -olefin copolymers, hydrogenated polyisoprenes, polyvinylidene fluorides, polytetrafluoroethylenes, polyesters, polyamides, polyacetals, and polystyrenes.
- 15
16. The method of Claim 13 wherein the low surface energy substrate is an isotactic polypropylene.



## ABSTRACT

The present invention relates to a 2-part adhesive formulation comprising, in the first part, water, a surfactant, and a protected alkylborane complex, and an acrylic monomer and a trialkylborane-displacing initiator in the second part. The formulation can be applied to a low surface energy substrate to make an effective adhesive without the aid of any surface pretreatment. The adhesive formulation can also be prepared by combining the complex with a mixture of the water, the surfactant, the monomer, as well as other additives and thixotropes, and applying the combination to the low surface energy substrate.

5